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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C11D 3/39	A1	(11) International Publication Number: WO 93/04159 (43) International Publication Date: 4 March 1993 (04.03.93)
(21) International Application Number: PCT/SE91/00895 (22) International Filing Date: 20 December 1991 (20.12.91) (30) Priority data: 9102380-4 16 August 1991 (16.08.91) SE (71) Applicant (for all designated States except US): KOMMEN- TUS ECOGREEN AKTIEBOLAG [SE/SE]; S-125 88 Älvsjö (SE). (72) Inventor; and (75) Inventor/Applicant (for US only) : LEJON, Ingemar [SE/ SE]; Starrängsringen 61, S-115 50 Stockholm (SE). (74) Agents: FOGELBERG, Lennart et al.; Stenhagen Patent- byrå AB, Box 17709, S-118 93 Stockholm (SE).		(81) Designated States: AU, CA, CS, FI, HU, JP, NO, PL, SU, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LU, MC, NL, SE). Published <i>With international search report.</i>
(54) Title: STABILIZING PERCARBONATE IN DETERGENTS (57) Abstract A method for stabilizing percarbonate in detergents is effected by: I) mixing components carriers, alkali donors, corrosion inhibitors, anticaking agents, sequestering agents and optional surfactants in the form of solid particles in a first stage; II) mixing in a second stage the solid particles from I) with liquid substances in droplet form so as to coat the surfaces of said particles with said substances, said substances comprising A) one or more amphoteric surfactants selected from tallow amphi-polycarboxy glycinate, mixed C8-amphocarboxylates, caprylo-amphocarboxy propionate, cocoamphocarboxy propionate and cocoamphocarboxy glycinate, and B) one or more nonionic surfactants, and optionally C) one or more anionic surfactants, wherein a sequestering agent capable of binding heavy metal ions, particularly Fe ²⁺ and Fe ³⁺ , has been dissolved in at least one of these liquid substances, and III) mixing percarbonate as a bleaching agent in a third stage, therewith to produce detergent powder.		

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STABILIZING PERCARBONATE IN DETERGENTSTechnical Field

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The present invention relates to a method of stabilizing percarbonate in powder detergents.

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The object of the invention is to provide a method by means of which the stability of percarbonate in detergents can be increased to a substantially greater extent than has hitherto been possible.

Background Art

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Sodium perborate is used as a bleaching agent in many laundry washing detergents at present available commercially. This compound, however, has a number of undesirable properties when used as a bleaching agent in detergents.

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Sodium perborate is a relatively stable chemical compound which results in a low bleaching effects when washing at temperatures of 30-40°C. From an environmental aspect, however, it is preferred to wash at lower temperatures, because of the resultant lower energy consumption.

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Perborates also include boron, which has a harmful influence on marine plants, among others, and is therefore less suitable for use, due to its negative influence on the environment.

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Attempts have been made to use other oxygen-producing compounds as detergent bleaching agents. Such compounds

are percarbonates, particularly sodium percarbonate which, as a result of its less stable structure, provides a bleaching effect at lower temperatures than sodium perborate.

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Alkali percarbonates, and in particular sodium percarbonate, contain no components which are detrimental to the environment when used normally, and are therefore preferred as bleaching agents to sodium perborate.

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However, due to its less stable structure, percarbonate causes product durability problems when used as a detergent bleaching agent. Degradation of percarbonate is namely accelerated in the presence of other substances, such as heavy metals, readily oxidizable substances and moisture. As a result, percarbonate degrades relatively quickly when in mixture with a detergent, which results in a poorer washing effect and therewith a highly limited stability in storage.

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Consequently, endeavours have earlier been made to stabilize percarbonate intended for use in detergents, although with varying results.

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For example, French Patent Specification No. 7 615 716 and Belgium Patent Specification Nos. 805 812, 810 288, 810 289, 813 645 and 845 014 suggest encapsulation of the percarbonate in different water-soluble salts during its manufacture.

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Furthermore, European Patent Specification No. 0 021 498 discloses the addition of hydroxy carboxyl polymers in the manufacture of percarbonate.

These methods, however, do not provide a percarbonate of desired stability for its use in detergents.

Disclosure of the Invention

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In accordance with the present invention, it has been found that percarbonate can be stabilized in detergents to a far greater extent than was hitherto possible by
a) selection of ingoing surfactants in a given manner,
10 b) selection of a given technique in detergent manufacture, c) the use of certain auxiliaries as further additives, and d) mixing of the detergent components in a given order.

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The inventive method is characterized by

- I) mixing component carriers, alkali donors, corrosion inhibitors, anticaking agents, sequestering agents and optional surfactants in the form of solid particles in a first stage;
 - 20 II) mixing in a second stage the solid particles from I) with liquid substances in droplet form so as to coat the surfaces of said particles with said substances, said substances comprising
 - 25 A) one or more amphoteric surfactants selected from tallow amphi-polycarboxy glycinate, mixed C8-amphocarboxylates, caprylo-amphocarboxy propionate, cocoamphocarboxy propionate and cocoamphocarboxy glycinate, and
 - 30 B) one or more nonionic surfactants, and optionally
 - C) one or more anionic surfactants,
- wherein a sequestering agent capable of binding heavy metal ions, particularly Fe^{2+} and Fe^{3+} , has
35 been dissolved in at least one of these liquid

substances, and

III) mixing percarbonate as a bleaching agent in a third stage, therewith to produce detergent powder.

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It will be evident from the above characteristic features that the inventive method is based on the known so-called agglomeration technique for the manufacture of powder detergents.

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This agglomeration technique involves mixing solid, powder particles with liquid substances in droplet form. Agglomeration enables powdered detergents to be produced in high litre-weights and at high active-substance concentration. These so-called compact detergents have many advantages over detergents that are manufactured in spray towers. The compact detergents greatly reduce the need for space in transportation and in storage facilities, shops and in the home. The amount of material required for packaging purposes is also greatly reduced, as is also the energy required for manufacture.

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The inventive method entails mixing the detergent components stepwise, with the exception of the percarbonate, so as to encapsulate those substances which have an unstabilizing effect on percarbonate, so that the substances obtain an outer surface which will counteract degradation. Upon completion of the encapsulation process, the requisite amount of percarbonate is added to the detergent. The percarbonate used is preferably one which has itself been subjected to a stabilizing process with the aid of an earlier known technique.

According to the inventive method, there is also used in stage II) a combination of certain liquid surfactants, namely amphoteric surfactants chosen from the group tallow ampho-polycarboxy glycinate, mixed C8-amphocarboxylates, cocoamphocarboxy propionate, etc. on the one hand, and one or more nonionic surfactants and optionally one or more anionic surfactants on the other hand. An important feature according to the invention in this respect is that there is added to one or more of these liquid surfactants a sequestering agent which is capable of binding heavy metal ions, particularly Fe^{2+} and Fe^{3+} -ions, such ions often being present as contaminants in those substances used in powder detergents.

It is also possible, in accordance with the invention, to also mix in stage I) one or more protective colloids, preferably carboxymethyl cellulose.

When practicing the inventive method, it is also possible to also mix in stage I) or III) granule encapsulated enzymes, an antioxidation agent having been dissolved in at least one of the surfactants in stage II).

The enzymes are preferably of the kind used conventionally in the manufacture of powdered detergents.

In this connection, the antioxidation agent used in stage II) may be a $(\text{C}_1\text{-C}_4)$ -alkyl ester of 3,4,5-trihydroxybenzoic acid, preferably ethyl 3,4,5-trihydroxybenzoate, and/or butylhydroxyanisole.

The amount of antioxidant used is normally from 0.005 to 0.03 percent by weight, preferably 0.005-0.01

percent by weight (all percentages given here and in the following relate to the total weight of the detergent).

5 In accordance with the present invention, soda, disilicates, silicates and sodium sulphate are preferably used as component carrier, alkali donor, corrosion inhibitor and anticaking agent. The amount of soda
10 concentration used is generally within the range of 20-40, preferably 25-35 percent by weight, whereas the concentration of disilicate + silicate used lies within the range of 5-25, preferably 10-15 percent by weight, and the concentration of sodium sulphate used lies
15 weight. The total concentration of these components is generally from 50-65 percent by weight.

When practicing the present invention, the sequestering agent used in stage I) may consist of one or more
20 substances taken from the group carboxylates, phosphates and polyacrylates. Preferably, sodium citrate and/or a mixture of sodium tartrate and potassium tartrate are used, it being possible to add these
25 substances as such to the system or to form said substances in situ from citric acid or tartaric acid added to the system in stage I).

When the sequestering agent used consists of one or more carboxylates, the sequestering agent will normally
30 be present in a concentration within the range of 5-25, preferably 5-20 percent by weight. A mixture of 15-18 percent by weight sodium citrate and 1-5 percent by weight Na/K-tartrate is preferred.

When a solid surfactant is used in stage I), the surfactant is preferably a nonionic surfactant, particularly a fatty alcohol ethoxylate having 16-18 C-atoms in the alcohol moiety and a degree of ethoxylation of 20-25 moles ethylene oxide units. The surfactant concentration is normally within the range of 0-7.5, preferably 2.5-5 percent by weight. It is also possible, however, to use other solid surfactants in this stage. The total concentration of solid components used in stage I) normally lies within the range of 70-85 percent by weight.

Of the liquid surfactants used in stage II), the amphoteric surfactants are chosen from the group tallow amphopolycarboxy glycinate, mixed C8-amphocarboxylates, caprylo-amphocarboxy propionate, cocoamphocarboxy propionate and cocoamphocarboxy glycinate.

Examples of tallow amphi-polycarboxy glycinate used in this context are such products as those retailed under the trade names Ampholak® 7TX and Beraid® 7557 from Berol Nobel, Stockholm, Sweden. Examples of mixed C8-amphocarboxylates which can be used with the inventive method is the product retailed under the trade name Miranol® JEM CONC from Miranol Chemical Company, Inc., South Brunswick (Dayton), NJ, U.S.A., while an example of the caprylo-amphocarboxy propionate is the product retailed under the trade name Miranol® J2M-SF CONC from Miranol Chemical Company, Inc., South Brunswick (Dayton), NJ, U.S.A. An example of cocoamphocarboxy glycinates which can be used is the product retailed under the trade name Miranol® C2M CONC from Miranol Chemical Company, Inc., South Brunswick (Dayton), NJ, U.S.A., whereas an example of the cocoamphocarboxy propionate used is the product retailed

under the trade name Miranol® C2M-SF CONC from Miranol Chemical Company, Inc., South Brunswick (Dayton), NJ, U.S.A.

5 The amphoteric surfactant or amphoteric surfactants is/are normally present in a concentration of 1-15, preferably 3-8 percent by weight.

10 The nonionic surfactant used in stage II) when practicing the inventive method suitably consists of one or more substances taken from the group fatty alcohol ethoxylates, fatty alcohol polyethylene-polypropylene glycol ethers and oxoalcohol polyethylene glycol ethers, which are liquid at room temperature. Fatty
15 alcohol ethoxylates and oxoalcohol ethoxylates are preferred in this connection, such oxyates having a carbon chain of 8-18, preferably 10-14, carbon atoms in the alcohol part and a degree of ethoxylation of 3-15, preferably 3-12 moles ethylene oxide units.

20 The nonionic surfactant concentration is normally within the range of 1-15, preferably 3-8 percent by weight.

25 When practicing the inventive method, conventional anionic surfactants can be used in the detergent, for example paraffin sulphonate and/or lauryl sulphate and/or lauryl ether sulphate. The anionic surfactant or surfactants is or are suitably present in a concentration of 0-15, preferably 0-5 percent
30 by weight and may be excluded to no detriment.

The surfactants are sprayed onto the mixture of solid components, advantageously in the order in which the anionic surfactants, when used, are sprayed first
35 either alone or in mixture with the amphoteric surfac-

tants, and the amphoteric surfactants are preferably sprayed before spraying the nonionic surfactants.

5 The sequestering agent capable of binding heavy metal ions and the antioxidation agents are preferably dissolved in that surfactant of the surfactants used which dissolves most of the substance concerned.

10 The sequestering agent used in this connection may, for example, be a sequestering agent on the basis of the tetrasodium salt of ethylenediaminetetraacetic acid (Na_4EDTA) having a specific ability to bind Fe^{2+} and Fe^{3+} -ions, or one or more substances taken from the group citrates, tartrates, gluconates and corresponding acids, 15 preferably sodium citrate and/or a mixture of sodium tartrate and potassium tartrate or the corresponding acid or acids.

In the former case, the sequestering agent is normally present in a concentration within the range of 20 0.05-0.15 percent by weight, preferably 0.05-0.10 percent by weight.

In the latter case, in which citrates, etc. are used, the sequestering agent is suitably present in a concentration of 0.2-1.0, preferably 0.2-0.6 percent by 25 weight.

When practicing the inventive method, dyes and/or perfumes may also be mixed with the detergent in conventional amounts. In this case, the mixing procedure 30 is effected with the addition of dyes and/or perfume in solid form in stage I), while liquid substances of this kind are added in stage II). Preferably, these substances are added solely in a solid form or solely 35 in a liquid form, although it is possible, of course,

to use both solid and with substances of this kind, in which case it is necessary to divide the substances in stages I) and II) in accordance with the aforesaid principle.

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The percarbonate mixed in stage III) is normally added to a concentration of 5-20, preferably 5-10 percent by weight. As previously mentioned, the percarbonate used is advantageously a percarbonate that has already been stabilized in conjunction with its manufacture.

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In addition to the percarbonate, a moisture-absorbing material may also be added in stage III), preferably a disilicate and/or soda. The amount of moisture-absorbing material supplied to this stage is normally from 0-15 percent by weight. When the moisture-absorbing material is disilicate, the disilicate is normally supplied to a concentration to 3-8 percent by weight.

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Enzymes encapsulated in granules can also be added in stage III) instead of in stage I).

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The invention will now be described in more detail with reference to a number of working embodiments, although it will be understood that these embodiments do not limit the invention in any way.

EXAMPLE

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General Procedure

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A number of detergent powders were produced in an agglomerator known as a Forberg mixer obtained from Halvor Forberg A/S, Larvik, Norway.

The solid components intended for the first stage (stage I in the table below) were mixed in the afore-

said agglomerator, said components being finely divided in air. Liquid surfactants, optionally having substances dissolved therein, were then sprayed in a second stage (stage II in the table) in a fine droplet form on the fluidized mixture of solid particles, wherein the anionic surfactant, when present, was sprayed first, the amphoteric surfactant was sprayed second and the nonionic surfactant was sprayed last in order to coat the solid particles mixed in stage I).. Finally, sodium percarbonate and, when used, a moisture-absorbing agent were admixed with the aforesaid mixture in a third stage (stage III in the table).

This method of carrying out the invention is considered to be the best mode contemplated at present.

The various examples are combined with the following table.

In the case of certain surfactants recited in the table, the number of carbon atoms in the alkyl part have been referenced "C" followed by the number of carbon atoms in question, while the number of ethylene oxide units have been referenced "EO" with the number of units concerned.

12

Table

Concentrations in % by weight
Example No.

Component	1	2	3	4	5	6	7	8
<u>Stage I</u>								
<u>Component Carrier, etc.</u>								
1. Disilicate (Sikalon® 2D, Woellner-Werke, Germany)	12.0	12.0	18.0	12.0	15.0	15.0	15.0	7.5
2. Sodium sulphate	11.81	12.8	9.49	9.1	8.81	9.84	6.61	5.0
3. Sodium carbonate (light soda)	30.0	30.0	32.5	32.5	30.0	32.5	32.5	40.0
<u>Sequestering Agent</u>								
4. Sodium citrate	17.5	16.0	16.0	17.5	12.5	16.0	17.5	17.5
5. Sodium-/potassium tartrate	2.5	2.5	2.5	2.5	5.0	2.5	2.5	1.5
<u>Protective Colloid</u>								
6. Carboxy methyl cellulose	2.0	2.0	2.0	1.0	1.0	2.0	2.0	1.5
<u>Granule Encapsulated Enzymes</u>								
7. Esperase (Novo Indus- tri A/S, Denmark)	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.4
8. Savinase (Novo Indus- tri A/S, Denmark)	0.3	0.3	-	0.3	0.3	-	-	0.4
9. Termamyl (Novo Indus- tri A/S, Denmark)	-	-	0.3	-	-	0.3	0.3	0.5
10. Lipolase (Novo Indus- tri A/S, Denmark)	-	0.2	0.2	0.2	0.3	-	0.2	0.3
<u>Solid Surfactant</u>								
11. Fatty alcohol ethoxylate (C 16-18, EO 25)	2.5	2.5	2.5	2.5	2.5	2.5	-	3.0

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Concentrations in % by weight
Example No.

Component	1	2	3	4	5	6	7	8
<u>Stage II</u>								
<u>Anionic Surfactants</u>								
12. Paraffin sulphonate (Marlon® PS60, Hüls, Germany)	-	-	-	5.0	-	-	-	3.0
13. Sodium lauryl sulphate	-	0.3	-	-	0.3	0.35	-	0.4
<u>Amphoteric Surfactants</u>								
14. Tallow amphopoly carboxy glycinate (Ampholak® 7TX, Berol Nobel, Sweden)	4.5	4.5	-	-	2.25	4.5	4.0	4.0
15. Mixed C8-amphocar- boxylates (Miranol® JEM CONC, Miranol Chem. Co., Inc., U.S.A.)	-	-	-	2.0	2.25	-	2.0	-
16. Caprylo amphocar- boxy propionate (Miranol J2M-SF CONC, Miranol Chem. Co., Inc., U.S.A.)	-	-	5.0	-	-	-	2.0	-
<u>Nonionic Surfactants</u>								
17. Fatty alcohol ethoxy- late, C13, EO 3	-	1.5	-	-	-	-	-	2.0
18. Fatty alcohol ethoxy- late, C13, EO 7	4.5	-	-	-	-	-	-	-
19. Fatty alcohol ethoxy- late, C13, EO 9	-	3.0	-	-	-	-	-	2.0
20. Fatty alcohol ethoxy- late, C13, EO 12	-	-	-	-	2.5	-	-	-
21. Fatty alcohol ethoxy- late, C11, EO 7	-	-	-	-	2.5	-	-	-
22. Oxoalcohol polyethy- lene glycol ether, C13, EO3	-	-	2.0	-	-	-	-	-
23. Oxoalcohol polyethy- lene glycol ether, C13, EO 7	-	-	-	3.0	-	4.5	6.0	-

SUBSTITUTE SHEET

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Component	Concentrations in % by weight Example No.							
	1	2	3	4	5	6	7	8
24. Oxalcohol polyethylene glycol ether, C13, EO 9	-	-	3.0	-	-	-	-	-
<u>Sequestering Agent</u>								
25. Na ₄ EDTA (Trilon®BVT, BASF, Germany)	0.08 ¹	0.08 ¹	-	0.08 ¹	-	-	0.08 ¹	-
26. Sodium citrate or citric acid	-	-	0.1 ¹	-	0.1 ¹	0.1 ¹	-	-
27. Sodium-/potassium tartrate or tartaric acid	-	-	0.1 ¹	-	0.1 ¹	0.1 ¹	-	0.2 ¹
<u>Antioxidant</u>								
28. Ethyl-3,4,5-trihydroxybenzoate (Progallin A, Nipa Laboratories, England)	0.01 ²	-	0.01 ²	0.01 ²	-	0.01 ²	-	0.01 ²
29. Propyl-3,4,5-trihydroxybenzoate (Progallin P, Nipa Laboratories, England)	-	0.01 ²	-	-	0.01 ²	-	0.01 ²	-
30. Butyl hydroxianisole	-	0.01 ²	-	0.01 ²	0.01 ²	-	-	-
<u>Stage III</u>								
31. Sodium percarbonate (Degussa, Germany)	6.0	6.0	6.0	6.0	10.0	6.5	6.0	10.0
<u>Moisture Absorbing Agent</u>								
32. Disilicate (Sikalon® 2D, Woellner-Werke, Germany)	6.0	6.0	-	6.0	5.0	3.0	5.0	2.5

Remarks Relating to the ExamplesExample 1

- (1) The sequestering agent is dissolved in component 18.
 (2) The antioxidant is dissolved in component 18.

Example 2

- (1) The sequestering agent is dissolved in component 14.
 (2) The antioxidants are dissolved in component 19.

Example 3

- (1) The sequestering agents are dissolved in component 15.
 (2) The antioxidant is dissolved in component 22.

Example 4

- (1) The sequestering agent is dissolved in component 15.
(2) The antioxidants are dissolved in component 23.

Example 5

- (1) The sequestering agents are dissolved in component 15.
(2) The antioxidants are dissolved in component 21.

Example 6

- (1) The sequestering agents are dissolved in component 14.
(2) The antioxidant is dissolved in component 23.

Example 7

- (1) The sequestering agent is dissolved in component 15.
(2) The antioxidant is dissolved in component 23.

Example 8

- (1) The sequestering agent is dissolved in component 14.
(2) The antioxidant is dissolved in component 17.

Stability tests

The stability of a detergent according to the invention prepared according to Example 8 was tested by measuring the percentage of active oxygen (as a measure of the sodium percarbonate content) using the following procedure:

About 0.2 g of sample was weighed accurately into a small glass sample cup. 100 ml of sulfuric acid solution (1:9) were charged into a 250 ml conical beaker and a 0.1 N potassium permanganate solution was added dropwise until the solution was coloured a faint pink. The glass sample cup and contents were then added to the beaker and swirling was performed to dissolve the contents. Titration with potassium permanganate solution was immediately performed to the re-appearance of the same faint permanent pink colour.

The active oxygen content was calculated according to the formula:

$$\text{Active oxygen} = \frac{A \times 0.08}{W} \% \text{ by weight}$$

wherein A is the weight of the sample (g) and A is the
5 titration (ml):

The following results were obtained from two samples (A
and B) taken from different batches.

10

	Time (days)	Active oxygen (% by weight) in sample	
		A	B
	0	1.11	1.09
	4	1.14	
15	12	1.2	
	16		1.08
	22	1.07	

20

25

C L A I M S

1. A method for stabilizing percarbonate in detergents, characterized by

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I) mixing component carriers, alkali donors, corrosion inhibitors, anticaking agents, sequestering agents and optional surfactants in the form of solid particles in a first stage;

10

II) mixing in a second stage the solid particles from I) with liquid substances in droplet form so as to coat the surfaces of said particles with said substances, said substances comprising

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A) one or more amphoteric surfactants selected from tallow amphoteric polycarboxy glycinate, mixed C8-amphocarboxylates, caprylic-amphocarboxy propionate, cocamphocarboxy propionate and cocoamphocarboxy glycinate, and

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B) one or more nonionic surfactants, and optionally

C) one or more anionic surfactants, wherein a sequestering agent capable of binding heavy metal ions, particularly Fe^{2+} and Fe^{3+} , has been dissolved in at least one of these liquid substances, and

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III) mixing percarbonate as a bleaching agent in a third stage, therewith to produce detergent powder.

30

2. A method according to Claim 1, characterized by also mixing one or more protective colloids, preferably carboxymethyl cellulose, in stage I).

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3. A method according to Claim 1 or 2, c h a r -
a c t e r i z e d by also mixing granule encapsulated
enzymes in stage I) or stage III), an antioxidant having been dis-
solved in at least one of the surfactants in stage II).

5

4. A method according to Claim 3, c h a r a c -
t e r i z e d by adding as the antioxidant in stage
II) a (C₁-C₃)-alkyl ester of 3,4,5-trihydroxybenzoic
acid, preferably ethyl 3,4,5-trihydroxybenzoate, and/or
butylhydroxyanisole.

10

5. A method according to one or more of Claims 1-4,
c h a r a c t e r i z e d by using soda, disilicates,
silicates and sodium sulphate as component carrier,
alkali donor, corrosion inhibitor and anticaking agent.

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6. A method according to one or more of Claims 1-5,
c h a r a c t e r i z e d by using as sequestering
agent in stage I) one or more substances taken from the
group carboxylates, phosphates and polyacrylates,
preferably sodium citrate and/or a mixture of sodium
tartrate and potassium tartrate.

20

7. A method according to one or more of Claims 1-6,
c h a r a c t e r i z e d in that the nonionic surfac-
tant used is one or more substances taken from the
group fatty alcohol ethoxylates, fatty alcohol poly-
ethylenepolypropylene glycol ethers and oxoalcohol
polyethylene glycol ethers.

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8. A method according to Claim 7, c h a r a c -
t e r i z e d in that the fatty alcohol ethoxylates
and oxoalcohol ethoxylates have a carbon chain contain-
ing 8-18, preferably 10-14 carbon atoms in the alcohol

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moity and a degree of ethoxylation of 3-15, preferably 3-12 moles ethylene oxide units.

9. A method according to one or more of Claims 1-8,
5 c h a r a c t e r i z e d by adding dyes and/or
perfume in solid form in stage I) or in liquid form in
stage II).
10. A method according to one or more of Claims 1-9,
10 c h a r a c t e r i z e d in that the sequestering
agent used in stage II) is a sequestering agent on the
basis of the tetrasodium salt of ethylenediaminetetra-
acetic acid having a specific ability to bind Fe^{3+} , or
one or more substances taken from the groups citrates,
15 tartrates, gluconates and corresponding acids, preferably
sodium citrate and/or a mixture of sodium tartrate and
potassium tartrate or the corresponding acid or acids.
11. A method according to one or more of Claims 1-10,
20 c h a r a c t e r i z e d by adding a moisture absorb-
ing material, preferably disilicate and/or soda in
stage III) in addition to the percarbonate.

INTERNATIONAL SEARCH REPORT

International Application No PCT/SE 91/00895

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 11 D 3/39																	
II. FIELDS SEARCHED <div style="text-align: right; font-size: small;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border: none;"> <tr> <td style="width: 25%; border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px;"> Classification System IPC5 </div> </td> <td style="border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px;"> Classification Symbols C 11 D </div> </td> </tr> </table> <div style="text-align: center; font-size: x-small; margin-top: 5px;"> Documentation Searched other than Minimum Documentation to the extent that such Documents are included in Fields Searched⁸ </div>			<div style="border: 1px solid black; padding: 5px;"> Classification System IPC5 </div>	<div style="border: 1px solid black; padding: 5px;"> Classification Symbols C 11 D </div>													
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SE,DK,FI,NO classes as above																	
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹ <table border="1" style="width: 100%; border-collapse: collapse; font-size: x-small;"> <thead> <tr> <th style="width: 10%;">Category *</th> <th style="width: 70%;">Citation of Document,¹¹ with indication, where appropriate, of the relevant passages¹²</th> <th style="width: 20%;">Relevant to Claim No.¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>DE, A1, 3337719 (COLGATE-PALMOLIVE CO.) 26 April 1984, see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>DE, A, 2420762 (E.I. DU PONT DE NEMOURS AND CO.) 7 November 1974, see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>EP, A1, 0024201 (THE CLOROX COMPANY) 25 February 1981, see the whole document --</td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">A</td> <td>GB, A, 1361708 (FMC CORPORATION) 31 July 1974, see the whole document -- -----</td> <td style="text-align: center; vertical-align: top;">1-11</td> </tr> </tbody> </table>			Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³	A	DE, A1, 3337719 (COLGATE-PALMOLIVE CO.) 26 April 1984, see the whole document --	1-11	A	DE, A, 2420762 (E.I. DU PONT DE NEMOURS AND CO.) 7 November 1974, see the whole document --	1-11	A	EP, A1, 0024201 (THE CLOROX COMPANY) 25 February 1981, see the whole document --	1-11	A	GB, A, 1361708 (FMC CORPORATION) 31 July 1974, see the whole document -- -----	1-11
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<div style="display: flex; justify-content: space-between; font-size: x-small;"> <div style="width: 45%;"> <p>* Special categories of cited documents:¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>																	
IV. CERTIFICATION <table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 18th September 1992 </div> </td> <td style="border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report 23 -09- 1992 </div> </td> </tr> <tr> <td style="border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center; font-weight: bold;">SWEDISH PATENT OFFICE</div> </div> </td> <td style="border: none; vertical-align: top;"> <div style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;"> Dagmar Järvman </div> </div> </td> </tr> </table>			<div style="border: 1px solid black; padding: 5px;"> Date of the Actual Completion of the International Search 18th September 1992 </div>	<div style="border: 1px solid black; padding: 5px;"> Date of Mailing of this International Search Report 23 -09- 1992 </div>	<div style="border: 1px solid black; padding: 5px;"> International Searching Authority <div style="text-align: center; font-weight: bold;">SWEDISH PATENT OFFICE</div> </div>	<div style="border: 1px solid black; padding: 5px;"> Signature of Authorized Officer <div style="text-align: center;"> Dagmar Järvman </div> </div>											
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**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/SE 91/00895**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the Swedish Patent Office EDP file on 28/08/92. The Swedish Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A1- 3337719	84-04-26	AU-B- 565445	87-09-17
		AU-D- 2026683	84-05-03
		BE-A- 898056	84-04-24
		CA-A- 1217402	87-02-03
		CH-A-B- 656144	86-06-13
		FR-A-B- 2534928	84-04-27
		GB-A-B- 2129456	84-05-16
		NL-A- 8303639	84-05-16
		SE-B-C- 461658	90-03-12
		SE-A- 8305765	84-04-22
		US-A- 4450089	84-05-22
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		FR-A-B- 2227320	74-11-22
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		AU-B- 465508	75-10-02
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		CA-A- 967728	75-05-20
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		FR-A-B- 2159301	73-06-22
		JP-C- 1019539	80-10-30
		JP-A- 48055197	73-08-02
		JP-B- 55010523	80-03-17
		NL-A- 7215062	73-05-11
		SE-B-C- 377104	75-06-23
		US-A- 3773678	73-11-20